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Structure and micromorphology of titanium dioxide nanoporous microspheres formed in water solution

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Abstract

TiO_2 nanoporous microspheres of 20 μm diameter with good crystallinity have been obtained by precipitation from aqua solution of ammonium titanate with nitric acid at pH = 1 and T = 100°C. Pure rutile, space group $P4_2/mnm$, phase composition has been confirmed by XRD analysis of the precipitate. SEM observation of these microspheres shows developed nanoporous structure with pore diameter of 20-30 nm.

Keywords: nanocrystal; nanoporous;TiO_2; rutile; precipitation

1. Introduction

Fabrication of mineral-like synthetic crystals in a nanosize range is a paramount task of modern materials science because of new interesting physiochemical parameters due to pronounced micro- and nano-morphology. Particular interest to nanoporous materials is appearing because of developed surface area by a lot of fine pores or tunnels imparting specific characteristics. Firstly, large interior surface is accessible for an interaction with gases and liquids so the conditions become favourable to heterophase chemical or biochemical reactions, adsorption, guest-host synthesis. Secondly, multiplied number

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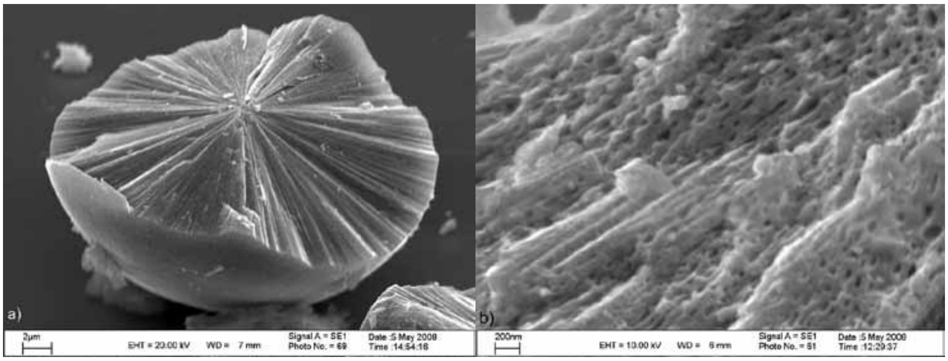

Fig. 1. (a) a split of TiO_2 microspheres; (b) porous structure of microspheres formed under conditions

of surface and subsurface atoms can extremely change the bulk characteristics of material.

Due to excellent chemical stability, titanium (IV) oxide is widely studied functional material. It has such potential applications as water-splitting catalyst, support for geteroneneous catalyst, electrode for solar cells, photodecomposition of hydrocarbon contaminations. Abundant phases of TiO2 are orthorhombic brookite, tetragonal anatase and rutile. Solution-phase obtaining of TiO_2 generally leads to anatase structure formation [1,2]. Several reports describe the brookite structure formation in strong acid solutions [3,4]. Present study is aimed to inquire into a potential of low-temperature aqueous solution way for obtaining of nanoporous TiO_2 microspheres with high-temperature rutile phase composition. The attraction of such structures is insolubility in typical solvents and stability of shape and phase under possible high-temperature using.

2. Experiment

Synthesis of TiO_2 microspheres was carried out by the two-stage synthesis. Firstly commercial TiO_2 (99.9%) was dissolved in the strong ammonia water solution under the stirring and heating at $T = 100^{o}C$. So prepared ammonium titanate solution with pH =14 was filtered with filter paper and acidated to pH = 1 with nitric acid under continuous stirring and heating at $T = 100^{o}C$. The final deposit was washed with distilled water up to pH = 6 of wash water and dried in air at room temperature. The phase composition was determined by powder x-ray diffraction (XRD) method. XRD patterns were collected on a Bruker

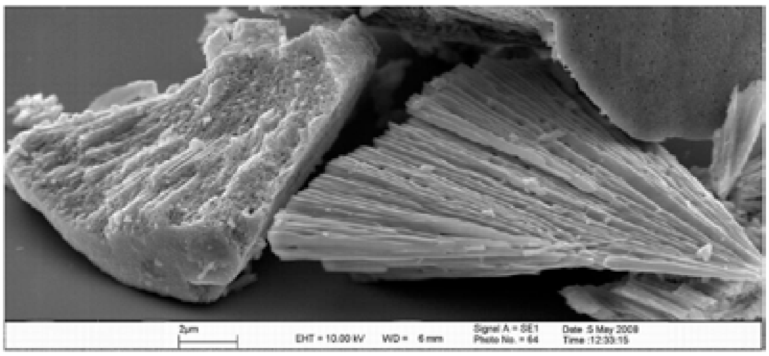

Fig. 2. Internal developed nanoporous structure of TiO_2 microspheres

X8APEX diffractometer (MoK_{α} radiation, graphite monochromator, 1024x1024 pixel resolution of the CCD detector, sample-to-detector distance L = 50.1 mm). The morphology of TiO_2 nanoporous microspheres crystals was examined by scanning electron microscopy (SEM) on a LEO 1430 device (CKP "Nanostructures"). The accelerating voltage of the electron gun was 10 kV. The chemical composition of the samples was determined by x-ray microanalysis. The results were either averaged over an area of 100x80 μm^2 or referred to individual microcrystals.

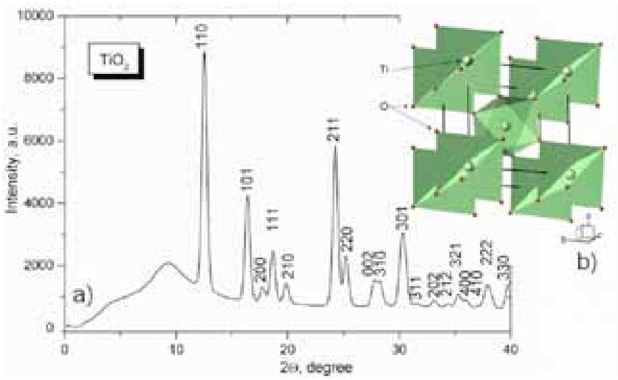

Fig. 3. (a) X-ray diffraction pattern obtained for the TiO_2 microspheres; (b) crystal structure of rutile phase

3. Results and discussions

As a result, white monosized microspheres with 20 μm typical diameter were fabricated. The SEM image of splits of these microspheres is shown on Fig. 1(a). The microspheres grown under the conditions contain developed nanoporous structure with very uniform pore size of 20 ÷ 30 nm shown in Fig. 1(b). As it is evident from Fig. 2, the pores are formed as a radial tunnels.

The X-ray diffraction pattern obtained for the TiO_2 microspheres is shown in Fig.3.a. All peaks are indexed within the tetragonal singony of rutile phase, space group $P4_2/mnm$, which crystal structure illustrated in Fig.3.b is formed by corner-bonded [TiO_6] octahedra. No foreign peaks are detected in the XRD pattern. Small amorphous halo over the $2\theta = 5 \div 15°$ region can be attributed to effect of sample grinding before XRD analysis. In Table 1 the set of interplanar spacing evaluated from the XRD pattern is compared with those of other known TiO_2 minerals. Comparison of tabulated data reveals that the phase composition of our sample is well related to high-temperature rutile phase ($P4_2/mnm$, PDF 21-1276, cell parameters: a = 4.593 Å, c = 2.959 Å) and confirms phase purity of synthesized nanoporous TiO_2 microsphere crystals.

4. Conclusions

The potentials of the water-solution way without additive thermal treatment for formation of TiO_2 nanoporous microspheres with high-temperature rutile phase composition have been demonstrated. Developed 20 ÷ 30 nm nanoporous structure of the microspheres would be interesting in various catalysis and photocatalysis applications. TiO_2 porous microspheres can be suitable for nanocomposite fabrications. This low-temperature solution method was previously applied for such simple oxides as h-WO_3, β-GeO_2 and h-MoO_3 [5,6]. Respectively, this method seems be enough universal to be developed for generation other simple and complex oxides because of a possibility for generation of equilibrium crystal form, accurate dimension control and doping promising for creation effective functional oxides.

Table 1. *d*-spacings (Å) for known TiO_2 minerals

Structural analog						This study
Unnamed mineral *C2/m*	Hongquiite *Fm3m*	Srilankite *Pbcn*	Brookite *Pcab*	Anatase $I4_1/amd$	Rutile $P4_2/mnm$	
PDF 35-0088	**PDF 29-1361**	**PDF 23-1446**	**PDF 29-1360**	**PDF 21-1272**	**PDF 21-1276**	
6.21_{60}						
3.56_{100}		3.50_{80}	3.51_{100}	3.51_{100}		
			3.46_{80}		3.24_{100}	3.24_{100}
3.11_{90}						
2.90_{60}		2.85_{100}	2.9_{90}			
2.45_{20}	2.47_{50}	2.47_{40}	2.47_{25}	2.43_{10}	2.48_{50}	2.48_{48}
2.37_{40}			2.37_{6}	2.37_{20}		
2.24_{18}		2.28_{10}	2.29_{5}		2.29_{8}	2.29_{5}
		2.17_{40}			2.18_{25}	2.18_{28}
	2.14_{100}	2.12_{60}	2.13_{16}			
2.07_{30}					2.05_{10}	2.05_{5}
2.02_{70}		2.01_{30}				
1.87_{60}			1.89_{30}	1.89_{35}		
		1.69_{60}	1.69_{20}	1.69_{20}	1.68_{60}	1.68_{66}
		1.66_{80}	1.66_{17}	1.66_{20}		
		1.64_{80}	1.64_{5}		1.62_{20}	1.62_{26}
1.60_{40}			1.60_{13}			
	1.53_{70}		1.54_{7}			
		1.49_{20}	1.49_{10}	1.49_{4}	1.47_{10}	1.47_{18}
			1.45_{12}		1.45_{12}	1.45_{18}
		1.42_{20}	1.43_{10}		1.42_{2}	
			1.36_{5}	1.36_{6}	1.35_{20}	1.35_{34}
		1.32_{5}	1.33_{8}	1.33_{6}	1.34_{12}	
					1.30_{2}	1.30_{1}
	1.29_{50}	1.27_{5}	1.28_{2}	1.27_{2}	1.27_{5}	
			1.23_{10}	1.26_{10}	1.24_{4}	1.24_{2}
			1.21_{2}	1.25_{4}	1.20_{2}	1.20_{1}
			1.15_{4}	1.18_{1}	1.17_{6}	1.17_{7}
			1.14_{2}	1.17_{2}	1.14_{4}	1.14_{4}
			1.12_{4}	1.16_{6}	1.11_{2}	1.11_{1}
			1.03_{3}	1.06_{2}	1.09_{8}	1.09_{16}
	1.08_{80}	1.08_{10}	1.02_{4}	1.05_{4}	1.08_{4}	1.08_{17}

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